MERCAPTANS AS REAGENTS FOR ISOLATION AND RESOLUTION OF α,β-UNSATURATED CARBONYL COMPOUNDS

BY

RICHARD HARVEY TENNYSON

B.S., St. Mary's College, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The ease with which mercaptans react with α,β-unsaturated compounds in the presence of basic catalysts to give good yields of the corresponding addition products has long been recognized. The additional reports of the ready reversibility of the reaction under a variety of conditions offer a means of isolation, purification, and resolution of the unsaturated compounds.

Recent investigations concerned with the chemistry of the terpenes (1,2) have emphasized the desirability of such a method, and this research was initiated in conjunction with attempts to develop a total synthesis of *dl*-pulegone. Successful completion of this synthesis necessitated development of a satisfactory method for purification of the reaction product.

The purpose of this investigation was the discovery of a mercaptan which would react by conjugate addition to α,β-unsaturated compounds to give good yields of solid sulfides. Benzalacetophenone, mesityl oxide, *d*-pulegone, ethyl acrylate, ethyl crotonate, and ethyl cinnamate were selected as trial compounds for the studies of the mercaptans. Piperidine was the catalyst of choice in most cases.

Discussion Of Results

In common with all the mercaptans investigated, thioglycolanilide gave a good yield of a solid sulfide with benzalacetophenone; however, its reactions with the other trial compounds produced viscous liquids which could neither be crystallized nor distilled. Thiophenol was more promising in that the liquid sulfides formed from it could be isolated and purified by distillation; yields of the thiophenyl derivatives were

generally good to excellent.

The derivatives of thiophenol which were investigated in the hope of obtaining solid sulfides included *p*-mercaptobenzoic acid, 1-(*p*-mercaptobenzoyl)-piperidine, and *m*-mercaptobenzoic acid. Of these mercaptans, only the last named showed promise. Its reactions with benzalacetophenone and ethyl acrylate produced excellent yields of solid sulfides, and a poor yield of a solid derivative was obtained with mesityl oxide.

Good yields of β-thio-(*m*-carboxyphenyl)-*sec*-butyl propionate were obtained from the reaction of *sec*-butyl acrylate with *m*-mercaptobenzoic acid, and a partial resolution of this sulfide was accomplished through the *d*-α-phenylethylamine salt.

d-Pulegone was isolated from pennyroyal oil through the intermediate 8-thiophenyl-*p*-menthane-3-one. The *d*-pulegone thus obtained was more nearly pure than that isolated through the bisulfite addition compound, but it still contained small amounts of contaminants.

A total synthesis of *dl*-pulegone was accomplished, and final purification of the product was achieved through the thiophenol adduct. Decarbonylation of the glyoxalate obtained by condensation of 3-methylcyclohexanone with ethyl oxalate produced fair yields of 2-carbethoxy-5-methylcyclohexanone. Treatment of the ketoester with methylmagnesium iodide first produced the halomagnesium enolate, and subsequent reaction at the ester group produced 8-hydroxy-*p*-menthane-3-one. Spontaneous dehydration to *dl*-pulegone was incomplete, and it was not possible to purify the product by distillation. Treatment of the mixture with thiophenol produced 8-thiophenyl-*p*-menthane-3-one, from which pure *dl*-pulegone was recovered in good yield.

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VITA

The author was born in Minneapolis, Minnesota, on October 11, 1921. He attended the parochial schools of that city and was graduated from De La Salle High School in June, 1939. In September of that year he entered St. Mary's College at Winona, Minnesota. In the fall of 1942, he was inducted into the Armed Forces of the United States. After three years of service in the American and European Theaters of Operations, he returned to St. Mary's College, where he received the degree of Bachelor of Science in June, 1946. He entered the Graduate College of the University of Illinois in September, 1946. He held a half-time teaching assistantship from September, 1946, through June, 1950.